09/762677
532 Rec'd PCT/PTO 12 FEB 2001

AM 1497

TUBE FOR TRANSPORTING PETROL

The present invention relates to tubes for transporting chemically aggressive fluids or solvents, particularly petrol, and especially for conveying the petrol from the tank of a motor vehicle to the engine.

For safety and environmental protection reasons, motor-vehicle manufacturers require these tubes to have both mechanical properties such as strength and flexibility with good cold (- 40°C) impact strength as well as good high-temperature (125°C) strength, and also very low permeability to the hydrocarbons and their additives, particularly alcohols such as methanol and ethanol. These tubes must also have good resistance to the fuels and lubrication oils for the engine.

Among the characteristics of the specification for these tubes, five are particularly difficult to obtain jointly in a simple manner:

- cold (- 40°C) impact strength according to the General Motor GM 213M test;
- fuel resistance (the fuel must not extract components from the tube);
- high-temperature (125°C) strength;
- very low permeability to petrol;
- good dimensional stability of the tube in use with the fuel, especially petrol.

In tubes of various structures, the cold impact strength remains unpredictable before having carried out the standardized tests for cold impact strength.

Moreover, it is already known from Patent Application EP 0,781,799 that in motor vehicles, under the effect of the injection pump, the petrol flows at high speed in the pipes connecting the engine to the tank. In certain cases, the friction between the petrol and the internal wall of the tube can generate electrostatic charges, the accumulation of which may result in an electrical discharge (a spark) capable of igniting the petrol with catastrophic consequences (an explosion). It is therefore necessary to limit the surface resistivity of the internal face of the tube to a value of generally less than or equal to 10^9 ohms/square and preferably less than or equal to 10^6 ohms/square. It is known to lower the surface resistivity of polymeric resins or materials by incorporating conductive and/or semiconductive materials into them, such as carbon black, steel fibres, carbon fibres, and particles (fibres, platelets or spheres) metallized with gold, silver or nickel.

Among these materials, carbon black is more particularly used, for economic and processability reasons. Apart from its particular electrically

conductive properties, carbon black behaves as a filler such as, for example, talc, chalk or kaolin. Thus, those skilled in the art know that when the filler content increases, the viscosity of the polymer/filler blend increases. Likewise, when the filler content increases, the flexural modulus of the filled polymer increases. These known and predictable phenomena are explained in "Handbook of Fillers and Reinforcements for Plastics", edited by H.S. Katz and J.V. Milewski - Van Nostrand Reinhold Company - ISBN 0-442-25372-9, see in particular Chapter 2, Section II for fillers in general and Chapter 16, Section VI for carbon black in particular.

As regards the electrical properties of carbon black, the technical report "KETJENBLACK EC - BLACK 94/01" by Akzo Nobel indicates that the resistivity of a formulation drops very suddenly when a critical carbon black content, called the percolation threshold, is reached. When the carbon black content increases further, the resistivity rapidly decreases until reaching a stable level (plateau region). It is therefore preferred, for a given resin, to operate in the plateau region in which a metering error will have only a slight effect on the resistivity of the compound.

Tubes for transporting petrol, having a structure comprising poly(vinylidene fluoride) (PVDF), are already known in the prior art.

Thus, EP 0,558,373 A2 describes a tube, based on polyamide, consisting of a polyamide outer layer and of a PVDF inner layer which are bonded together by an adhesion binder. By virtue of its PVDF inner layer with a thickness of 250 μm, this tube has very good impermeability to hydrocarbons and to their additives and does not exhibit the phenomenon of extraction of its constituents by dynamic contact with the fuel, since PVDF does not contain extractable compounds.

However, this known tube has insufficient impact strength in the GM 213M test, the actual test being more severe than the - 40°C impact strength tests according to the DIN 73378 standard or according to the DIN 53453 standard.

International Application WO 94/25524 describes a polyamide-based multilayer tube consisting of an outer layer made of polyamide, of an inner layer made of fluoro polymer, especially PVDF, and of an adhesion binder based on a polymer A having glutarimide, glutaric anhydride, carboxylic acid and carboxylic ester groups.

International Application WO 95/11947 describes a petrol tube comprising a PVDF inner layer, a polyamide outer layer and an adhesion binder layer based on a polymer A comprising glutaric anhydride, carboxylic acid and carboxylic ester groups.

European Patent 0,637,511 B describes a multilayer thermoplastic composite containing:

I. at least one layer based on a moulding compound consisting of polyamide; and

II. at least one layer adjacent to the layer I, based on a moulding compound consisting of a blend of:

a) poly(vinylidene fluoride) and

b) polyglutarimide,

the layers being bonded together by dynamic bonding.

However, in order to increase the cold impact strength, provision is made for the polyglutarimides to also contain impact modifiers, for example core/shell polymers having a core made of poly(butyl acrylate) and a shell made of poly(methyl methacrylate) and/or polyglutarimide. This patent does not describe the impact strength behaviour of these structures, particularly in the GM 213M test.

Moreover, H. Ries in "Multilayer-Plastics Fuel Lines", Kunststoffe 85 (1995) 11, pp. 1933-1936" states that the best barrier effect is obtained when the petrol is in direct contact with the barrier layer (made of PVDF) but that such tubes are not used since they do not have the low-temperature impact strength of PA-12.

A first objective of the present invention is to obtain a tube intended to transport chemically aggressive fluids or solvents, particularly petrol and its additives, and having to withstand the GM 213M impact test while still exhibiting excellent barrier properties with respect to these fluids or solvents.

The Applicant has found that, at the date of the present patent application, there was no tube structure which withstands the GM 213M test and the internal layer of which, intended to be in contact with chemically aggressive fluids or solvents, particularly petrol, is based on a fluoro polymer.

A second objective of the present invention is to obtain a tube having the same properties as that above apart from the fact that its inner layer intended to come into contact with petrol is electrically conductive.

The first objective is obtained by a tube having in its radial direction, from the inside to the outside, a so-called inner layer based on a fluororesin (or fluoro polymer) and intended to come into contact with a flowing fluid, characterized in that the inner layer is formed from a blend comprising a semicrystalline thermoplastic fluororesin and an ABC triblock copolymer, the three blocks A, B and C being linked together in this order, each block being either a homopolymer or a copolymer obtained from two or more monomers, the A block being linked to the B block and the B block to the C block by means of a covalent bond or of an intermediate molecule linked to one of these blocks via a covalent bond and to the other block via another covalent bond, and in that:

- the A block is compatible with the fluororesin;
- the B block is incompatible with the fluororesin and is incompatible with the A block, and
- the C block is incompatible with the fluororesin, the A block and the B block.

The tube thus obtained withstands the GM 213M impact test while still exhibiting excellent barrier properties with respect to petrol and to its additives.

Advantageously, the tube is a bilayer and comprises an outer layer made of polyamide or of a polyamide/polyolefin blend having a polyamide matrix, the inner layer and the polyamide or polyamide-matrix layer being fastened together.

Advantageously, the tube is a bilayer and comprises an outer layer made of polyamide or of a polyamide/polyolefin blend having a polyamide matrix, the inner layer and the polyamide or polyamide-matrix layer being fastened together by the addition of a functional acrylic compound to the blend of the inner layer.

In general, the tube is a trilayer and comprises an outer layer made of polyamide or of a polyamide/polyolefin blend having a polyamide matrix, the inner layer and the polyamide or polyamide-matrix layer being fastened together by an adhesion binder placed between them.

Preferably, the tube is a multilayer and comprises a layer made of polyamide or of a polyamide/polyolefin blend having a polyamide matrix, the inner layer and the polyamide or polyamide-matrix layer being fastened together by a succession of intermediate layers, each of which is fastened to its adjacent layers.

The second objective of the present invention is achieved by such a tube, which is characterized in that the blend of the inner layer contains a dispersed electrically conductive carbon black filler in an amount sufficient to give this inner layer a surface resistivity of less than or equal to 10^9 $\Omega/\square$ and preferably less than or equal to 10^6 $\Omega/\square$

Preferably, the layer which follows the carbon-black-filled inner layer, in a radial direction of the tube, from the inside to the outside, is of the same polymeric nature but does not contain an electrically conductive filler or an electrically significant amount of carbon black. The term "electrically significant amount" should be understood to mean an amount such that it produces a surface resistivity on the tube of less than or equal to 10^9 $\Omega/\square$.

The above expression "same polymeric nature" means that it is predominantly, by weight, a semicrystalline fluoro polymer, it being possible for this polymer also to be blended with an ABC triblock and even to have the

identical composition to the composition of the inner layer, without however containing a significant amount of carbon black.

The electrically conductive tubes thus obtained withstand the GM 213M impact test, while still maintaining excellent barrier properties with respect to petrol and to its additives, and do not have extractables.

The A block of an ABC copolymer is regarded as being compatible with the fluororesin if the A polymer identical to this block (and therefore without B and C sequences) is compatible with this resin in the melt. Likewise, the A and B blocks are regarded as being compatible if the A and B polymers identical to these blocks are compatible. In general, compatibility between two polymers should be understood to mean the ability of one to dissolve in the other in the melt, or else their complete miscibility.

If this is not the case, the polymers or blocks are called incompatible.

The lower the enthalpy of mixing of two polymers, the greater their compatibility. In some cases, there is a favourable specific interaction between the monomers which results in a negative enthalpy of mixing for the corresponding polymers. In the context of the present invention, it is preferred to use compatible polymers whose enthalpy of mixing is negative or zero.

However, the enthalpy of mixing cannot be conventionally measured for all polymers, and therefore the compatibility can only be determined indirectly, for example by viscoelastic analytical measurements in torsion or in oscillation, or else by differential calorimetry.

For compatible polymers, two glass transition temperatures or T_gs can be detected for the blend: at least one of the two T_gs is different from the T_gs of the pure compounds and lies within the temperature range between the two T_gs of the pure compounds. A blend of two completely miscible polymers has a single T_g.

Other experimental methods may be used to demonstrate the compatibility of the polymers, such as turbidity measurements, light-scattering measurements and infrared measurements (L. A. Utracki, Polymer Alloys and Blends, pp. 64-117).

Miscible or compatible polymers are listed in the literature - see, for example J. Brandrup and E.H. Immergut : Polymer Handbook, 3rd Edition, Wiley & Sons 1979, New York 1989, pp. VI/348 to VI/364; O. Olabisi, L. M. Robeson and M. T. Shaw : Polymer Miscibility, Academic Press, New York 1979, pp. 215-276; L.A. Utracki : Polymer Alloys and Blends, Hanser Verlag, Munich 1989. The lists appearing in these references are given by way of illustration and are not, of course, exhaustive.

Advantageously, the fluororesin is chosen from:

- homopolymers and copolymers of vinylidene fluoride (VF2) preferably containing at least 50% by weight of VF2 and at least one other fluoromonomer, such as chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE);

- homopolymers and copolymers of trifluoroethylene (VF3);

- copolymers, and especially terpolymers, combining the residues of chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE) or hexafluoropropylene (HFP) units and/or ethylene and possibly VF2 and/or VF3 units.

Preferably, the fluororesin is poly(vinylidene fluoride) (PVDF).

Advantageously, the PVDF has a viscosity ranging from 100 Pa.s to 2000 Pa.s, the viscosity being measured at 230°C, with a shear rate of 100 s^{-1}, using a capillary rheometer. These PVDFs are in fact particularly well suited to coextrusion as a blend with ABC triblocks.

Preferably, the PVDF has a viscosity ranging from 300 Pa.s to 1200 Pa.s, the viscosity being measured at 230°C, with a shear rate of 100 s^{-1}, using a capillary rheometer.

Thus, the PVDF sold under the trademark KYNAR® 710 having a viscosity ranging from 400 to 500 Pa.s is very well suited to coextrusion when it is blended with the ABC triblocks. This viscosity is measured in the same way as previously.

The block copolymer comprising at least three blocks A, B and C is such that the A block is linked to the B block and the B block to the C block by means of one or more single covalent bonds. In the case of several covalent bonds, between the A block and the B block and/or between the B block and the C block, there may be a single unit or a linked sequence of units serving to join the blocks together. In the case of a single unit, the latter may come from a monomer, called a moderator, used in the synthesis of the triblock. In the case of a linked sequence of units, this may be an oligomer resulting from the linking of monomer units of at least two different monomers in an alternating or random order. Such an oligomer may link the A block to the B block, and the same oligomer or a different oligomer may link the B block to the C block.

Preferably, the B block has a glass transition temperature $T_{g(B)}$, measured by differential thermal analysis, ranging from -100°C to -50°C. Thus, the B block then being thermoplastic in nature because of the existence of a glass transition temperature, this low $T_{g(B)}$ gives the B block elastomeric properties at - 40°C, which is the temperature of the GM 213M impact test.

Advantageously, the B block is chosen from polydienes, especially polybutadiene, polyisoprene and their random copolymers, or else from polydienes,

especially polybutadiene, polyisoprene and their random copolymers, that are partially or completely hydrogenated.

Preferably, the B block is a polybutadiene block having a glass transition temperature $T_{g(B)}$, measured by differential thermal analysis, ranging from -100°C to -50°C.

Preferably, the C block has a glass transition temperature $T_{g(C)}$ or a melting point $T_{m(C)}$ greater than $T_{g(B)}$ of the B block.

This characteristic means that the C block can either be in the glassy state or in a partially crystalline state and the B block is in the elastomeric state, for the same service temperature T_S.

According to the present invention, it is possible to choose the nature of the B blocks in order to have a certain defined $T_{g(B)}$ and thus, at the service temperature T_S of the material or of the article formed from the blend, and to have these B polymer blocks in an elastomeric or flexible state. On the other hand, since the C polymer blocks can have a $T_{g(C)}$ or a T_m greater than $T_{g(B)}$, they may be in a relatively rigid glassy state at the same service temperature.

Since the C blocks are incompatible with the thermoplastic resin(s), the A blocks and the B blocks, they form a rigid discrete phase within the material, forming nanodomains included in the material and serving as anchoring in the region of one of the ends of each B block. The other end of each B block is linked to an A block which has a strong affinity with the semicrystalline thermoplastic resin(s). This strong affinity provides a second anchoring in the region of the second end of the B block.

Advantageously, the A block is chosen from homopolymers and copolymers of alkyl (alkyl)acrylates, for example methyl methacrylate (MMA) and/or methyl or ethyl acrylate and/or those deriving from vinyl acetate.

Advantageously, the A block is poly(methyl methacrylate) (PMMA).

Preferably, this PMMA is syndiotactic and its glass transition temperature $T_{g(A)}$, measured by differential thermal analysis, is from +120°C to +140°C.

The triblocks which contain sequences deriving from alkyl (alkyl)acrylates may especially be prepared by anionic polymerization, for example using the processes described in Patent Applications EP 524,054 and EP 749,987.

Advantageously, the C block is chosen from styrene or α-methylstyrene homopolymers or copolymers.

Preferably, the ABC triblock is poly(methyl methacrylate-*b*-butadiene-*b*-styrene).

Advantageously, the blend of the semicrystalline thermoplastic fluororesin and the ABC triblock copolymer, possibly with the by-products of its

synthesis, contains at least 50% and preferably from 70 to 97% by weight of semicrystalline thermoplastic fluororesin(s) and the balance (to 100%) by weight of the triblock copolymer of number-average molecular mass (M_n) greater than or equal to 20,000 $g.mol^{-1}$, and preferably between 50,000 and 200,000 $g.mol^{-1}$, possibly with its by-products, consisting of:

- 20 to 93 and preferably 30 to 70 parts by weight of A sequences,
- 5 to 68 and preferably 10 to 40 parts by weight of B sequences,
- 2 to 65 and preferably 5 to 40 parts by weight of C sequences,

the percentages being calculated with respect to the total weight of fluororesin(s) with the block copolymer and possibly its by-products, without taking into account in these percentages the optional presence of other additives.

Advantageously, the blend of the semicrystalline thermoplastic fluororesin and the ABC triblock copolymer has a viscosity at 230°C, for a rate of 100 s^{-1}, ranging from 200 Pa.s to 4000 Pa.s. Preferably, this viscosity ranges from 300 Pa.s to 2000 Pa.s.

Advantageously, the blend is characterized in that it comprises poly(vinylidene fluoride) (PVDF) as thermoplastic fluororesin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

The Applicant has surprisingly discovered that, in the case of triblocks, the by-products resulting from the synthesis, such as diblocks or homopolymers, were not prejudicial to the mechanical properties of the blend according to the present invention, unlike the compositions of the prior art based on a diblock and PVDF. In the case of the latter known compositions, the presence of these homopolymers is particularly detrimental to the properties of the material and therefore absolutely requires an expensive purification operation.

Thus, the blend according to the invention comprising an ABC triblock copolymer may contain, as by-products of its synthesis, a BC diblock copolymer and possibly the C homopolymer.

Likewise, the blend according to the invention comprising an ABC triblock copolymer may contain, as by-products of its synthesis, an AB diblock copolymer and possibly the A homopolymer.

This is because the synthesis of a triblock copolymer is preferably carried out by successively joining together the A block to the B block and then to the C block, or conversely the C block to the B block and then to the A block, depending on the nature of the three blocks A, B and C, the A block being by definition the one which is compatible with the semicrystalline fluororesin.

The blend may also contain symmetrical linear or star-shaped block copolymers of the ABA or CBC type.

Advantageously, per 100 grams of a blend of fluoro polymer and ABC triblock copolymers, which contains 100-x grams of fluoro polymer and x grams of ABC triblock copolymers, the total amount by weight of these A and C homopolymers or AB, BC, ABA and CBC block copolymers is less than 3 times the amount x of ABC triblocks contained in the blend.

The blends according to the invention may also contain various additives and/or fillers and/or dyes and/or pigments, whether organic or mineral and whether or not macromolecular, well known in the literature.

By way of non-limiting examples of fillers insoluble in these blends, mention may be made of mica, alumina, talc, titanium dioxide, carbon black, especially electrically conductive carbon black, glass fibres, carbon fibres and macromolecular compounds.

By way of non-limiting examples of additives, mention may be made of UV stabilizers, fire retardants and processing aids.

The sum of these various additives and fillers represents in general less than 20% of the total mass of the blend of thermoplastic fluororesin with the ABC triblock and its associated homopolymers and/or copolymers mentioned above.

The term "polyamide" should be understood in the context of the present invention to mean polyamides or PAs which contain aliphatic and/or cycloaliphatic and/or aromatic units.

Mention may be made of polyamides obtained by polycondensation of one or more lactams or of α,ω-amino acids, preferably 10-aminododecanoic, 11-aminoundecanoic and 12-aminododecanoic acids.

The aliphatic diamines are α,ω-diamines containing, between the terminal amino groups, at least 6, and preferably from 6 to 10, carbon atoms. The carbon chain may be linear (polymethylenediamine) or branched, or else cycloaliphatic. Preferred diamines are hexamethylenediamine (HMDA), dodecamethylenediamine and decamethylenediamine.

The dicarboxylic acids may be aliphatic, cycloaliphatic or aromatic. The aliphatic dicarboxylic acids are α,ω-dicarboxylic acids having at least 4, and preferably at least 6, carbon atoms (not including the carbon atoms of the carboxylic groups) in the linear or branched carbon chain. The diacids are azelaic, sebacic and 1,12-dodecanoic acids. By way of illustration of such PAs, mention may be made of:

- poly(hexamethylene sebacamide) (PA-6,10);
- poly(hexamethylene dodecanediamide) (PA-6,12);
- poly(undecanoamide) (PA-11);
- poly(laurolactam) or poly(2-azacyclotridecanone) (PA-12);
- poly(dodecamethylene dodecanediamide) (PA-12,12);

- poly(caproamide) (PA-6);

- poly(hexamethylene adipamide) (PA-6,6).

The PAs have a number-average molecular mass M_n generally greater than or equal to 5000. Their inherent viscosity (measured at 20°C for a specimen of 0.5 g in 100 g of metacresol) is generally greater than 0.7.

Advantageously, nylon-11 or nylon-12 is used. Advantageously, the polyamide of the outer layer is plasticized by standard plasticizers such as n-butyl benzene sulphonamide (BBSA) and polymers comprising polyamide blocks and polyether blocks. These block polymers result from the condensation of polyamide blocks having carboxylic end groups with either polyetherdiols or polyetherdiamines, or a blend of these polyethers. This outer layer may also contain antioxidants and standard fillers such as carbon black. In general, the plasticizers of the polyamide-block and polyether-block type, which may be added to the outer layer, are those described in Patent Application FR 94/14521.

The expression "polyamide matrix" should be understood to mean products of the condensation:

- of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids or of one or more lactams, such as caprolactam, oenantholactam and laurolactam;

- of one or more salts or mixtures of diamines such as hexamethylenediamine, dodecamethylenediamine, metaxylylenediamine, bis(p-aminocyclohexyl)methane and trimethylhexamethylenediamine with diacids such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic and dodecanedicarboxylic acids;

or mixtures of all these monomers, which lead to copolyamides.

Polyamide blends may be used. Advantageously, PA-6 and PA-6,6 and PA-12 are used.

Polyolefins should be understood to mean polymers comprising olefin units such as, for example, ethylene, propylene and 1-butene units, and their higher homologues:

By way of examples, mention may be made of:

- polyethylene, polypropylene and copolymers of ethylene with α-olefins, these products possibly being grafted by unsaturated carboxylic acid anhydrides, such as maleic anhydride or unsaturated epoxides, such as glycidyl methacrylate;

- copolymers of ethylene with at least one product chosen from (i) unsaturated carboxylic acids, their salts and their esters, (ii) vinyl esters of saturated carboxylic acids, (iii) unsaturated dicarboxylic acids, their salts, their esters, their half-esters and their anhydrides and (iv) unsaturated epoxides, these

ethylene copolymers possibly being grafted by unsaturated dicarboxylic acid anhydrides or unsaturated epoxides:

- styrene/ethylene-butylene/styrene block copolymers (SEBS), optionally maleized.

Blends of two or more of these polyolefins may be used.

It is advantageous to use:

- polyethylene;
- polypropylene;
- copolymers of ethylene with an α-olefin;
- ethylene/alkyl (meth)acrylate copolymers;
- ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, the maleic anhydride being grafted or copolymerized;
- ethylene/alkyl (meth)acrylate/glycidyl methacrylate copolymers, the glycidyl methacrylate being grafted or copolymerized.

In order to facilitate the formation of the polyamide matrix, and if the polyolefins have few or no functional groups able to facilitate the compatibilization, it is recommended to add a compatibilizer.

The compatibilizer is a product known per se for compatibilizing polyamides and polyolefins.

As examples, mention may be made of:

- polyethylene, polypropylene, ethylene-propylene copolymers and ethylene-butylene copolymers, all these products being grafted by maleic anhydride or glycidyl methacrylate;
- ethylene/alkyl (meth)acrylate/maleic anhydride copolymers, the maleic anhydride being grafted or copolymerized;
- ethylene/vinyl acetate/maleic anhydride copolymers, the maleic anhydride being grafted or copolymerized;
- the above two copolymers in which the maleic anhydride is replaced with glycidyl methacrylate;
- ethylene/(meth)acrylic acid copolymers and possibly their salts;
- polyethylene, polypropylene or ethylene-propylene copolymers, these polymers being grafted by a product having a site which reacts with amines, these grafted copolymers then being condensed with polyamides or polyamide oligomers having a single amine end group.

These products are described in Patents FR 2,291,225 and EP 342,066, the contents of which are incorporated in the present application.

The amount of polyamide forming the matrix in the inner layer may be between 50 and 95 parts per 5 to 50 parts of polyolefin.

The amount of compatibilizer is the amount sufficient for the polyolefin to be dispersed in the form of nodules in the polyamide matrix. It may represent up to 20% by weight of the polyolefin. These polymers of the inner layer are manufactured by blending the polyamide, the polyolefin and optionally a compatibilizer using the standard melt-blending techniques (twin-screw, Buss, single-screw extruders).

Advantageously, the layer containing polyamide forms a nylon-6 (PA-6) or nylon-6,6 (PA-6,6) matrix in which either nodules of a blend of low-density polyethylene and of an ethylene/alkyl (meth)acrylate/maleic anhydride copolymer or an ethylene/alkyl (meth)acrylate/glycidyl methacrylate copolymer, or nodules of polypropylene are dispersed.

Such products are described in Patents US 5,070,145 and EP 564,338.

In the case of polypropylene, a compatibilizer is added which is advantageously an ethylene/propylene copolymer predominantly, by number, propylene units, this copolymer being grafted by maleic anhydride and then subsequently condensed with monoamine oligomers of caprolactam.

The binder layer makes it possible to achieve good adhesion between the polyamide layer or the layer made of the polyamide/polyolefin blend with a polyamide matrix and the inner layer made of the blend of fluoro polymer and ABC triblock optionally filled with electrically conductive carbon black.

By way of example of a binder, mention may be made of:

a binder as described in Patent Application EP 0,816,460 A1.

The binder may be chosen from the grafted polymers mentioned above and some of these are sold by Elf Atochem S.A. under the trademark OREVAC®.

The PA/PE blend with a PA matrix may be chosen from products sold by Elf Atochem S.A. under the trademark ORGALLOY®.

Thus, by way of example, a tube according to the present invention may be produced which has the following structure:

PA/binder/fluoro polymer + ABC triblock possibly with its synthesis by-products.

Advantageously, the inner layer filled with electrically conductive carbon black has a thickness ranging from 25 to 400 μm and preferably from 75 to 200 μm.

The next layer towards the outside, which does not contain electrically conductive carbon black or contains it not in an electrically significant amount, generally has a thickness of at least 50 μm and preferably of 50 to 500 μm.

The binder layer has a thickness generally of at least 10 μm and preferably from 25 to 100 μm.

The next layer(s) towards the outside generally has (have) a total thickness of at least 300 μm and preferably from 400 to 800 μm.

Preferably, the tube according to the present invention is characterized by:

an outside diameter ranging from 6 to 12 mm and a total thickness of 0.495 mm to 1.90 mm;

a thickness of 25 to 300 μm for the inner layer filled with electrically conductive carbon;

a thickness of 50 to 500 μm for the intermediate layer;

a thickness of 20 to 100 μm for the binder layer; and

a thickness of 400 to 800 μm for the outer layer or the other layers.

These multilayer tubes may be cylindrical, of constant external diameter, or annulate.

The tubes of constant external diameter may be manufactured in a conventional manner by coextrusion.

Conventionally, these tubes may include protective sheaths, especially made of rubber, in order to protect them from hot spots in the engine.

As regards the tubes used as hoses in service stations, the outside diameter is generally from 20 to 120 mm and their thickness from 0.8 to 14 mm. The binder thickness and the inner-layer thickness remain identical to those mentioned above. The tubes may be reinforced by any standard method.

The present invention will be more clearly understood with the aid of the following experimental part given solely by way of illustration of the present invention.

Experimental part:

Products used:

- PVDF

The commercial products (from Elf Atochem) sold under the trademark KYNAR® are VF2-based homopolymers or copolymers.

KYNAR®710 is a PVDF homopolymer available in granule form; its melting point is 170°C and its viscosity measured using a capillary rheometer at 230°C and 100 s^{-1} is between 400 and 700 Pa.s.

KYNAR®720 is a PVDF homopolymer available in granule form; its melting point is 170°C and its viscosity measured using a capillary rheometer at 230°C and 100 s^{-1} is between 750 and 1050 Pa.s.

KYNAR®740 is a PVDF homopolymer available in granule form; its melting point is 170°C and its viscosity measured using a capillary rheometer at 230°C and 100 s^{-1} is between 1500 and 2250 Pa.s.

- PVDF plasticizer: dibutyl sebacate

- PA

PA-12: The polyamide used is a commercial polyamide 12 (nylon-12) from Elf Atochem, with the reference MA 4411. This product consists of:

- 85% of polyamide 12 having an inherent viscosity of 1.65;
- 7% of n-butyl benzenesulphonamide (BBSA) which is a plasticizer;
- 6% of a thermoplastic elastomer based on a polyether-block-amide, having a Shore D hardness of 55 and a melting point of 159°C;
- 2% of additives (black colorants, lubricants, stabilizers).

- Impact modifier: EXL3600, which is an impact modifier of the MBS type, having a core/shell structure and sold by Rohm and Haas. It is based on methyl methacrylate-butadiene-styrene.

- Binder:

The product used, called Binder 1, is a binder based on KYNAR®720 containing especially MBS additives and other additives such as those described in Elf Atochem patents (Patents WO 94/25524 and WO 95/11947). It comprises:

- 50% of KYNAR®720 PVDF;
- 35% of EXL3600;
- 15% of a functional acrylic, this being an MMA copolymer and less than 5% of methacrylic acid and of glutaramic anhydride.

This binder makes it possible to achieve excellent adhesion between a polyamide layer and a PVDF layer.

- Carbon black:

This is sold by 3M under the name "Ensaco 250 Granular" and is characterized by a DBP absorption of approximately 190 ml/g and by a BET surface area of approximately 35 m^2/g.

- Triblock:

A triblock denoted by PMMA-PB-PS corresponds to a poly(methyl methacrylate-*b*-butadiene-*b*-styrene) triblock terpolymer.

Example 1

A PMMA-PB-PS triblock, with the reference ABC1 (58-20-22) has the following characteristics: the number-average molecular mass (M_n) of the PMMA blocks is 65,700 g.mol^{-1}, the M_n of the PB blocks is 22,800 and that of the PS blocks is 25,000. The PMMA block represents 58%, as mass fraction, of the total mass of the triblock, the PB block represents 20%, as mass fraction, of the total mass of the triblock and the PS block represents the remaining 22%. It is prepared using the operating method described in EP 524,054 or in EP 749,987.

The product obtained, ABC1* contains, in addition to the ABC1 triblock, a certain amount of BC1 diblock which is an intermediate of the synthesis; the BC1 diblock has a PS block of 25,000 M_n and a PB block of 22,800 M_n. The composition of the ABC1* product is 60% by mass of ABC1 triblock and 40% by mass of BC1 diblock. During the synthesis of the ABC1 triblock, a certain amount of the BC1 diblock is removed during synthesis so as to be used in certain formulation examples.

Processing of the blends:

The PVDF granules and the granules of the ABC1* product are dry-blended and introduced into a mixer of the melt-cokneader type of the BUSS brand, the diameter of the mixing screw of which is 46 mm. The conversion temperature is 230°C, with a material throughput of 15 kg/hour.

Various formulations of PVDF blends with a triblock or with other additives are produced according to this protocol – for the complete list, refer to Table I.

Table I

Compositions produced

Reference	PVDF	Additive	Composition as mass fraction	Viscosity at 230°C (Pa.s)
Control 1	KYNAR®710	ABC1* triblock	100/0	400-500
Formulation 1	KYNAR®710	ABC1* triblock	85/15	700-800
Formulation 2	KYNAR®710	ABC1* triblock	75/25	900-1000
Control 2	KYNAR®710	BC1 diblock	75/25	700-800
Control 3	KYNAR®720	ABC1* triblock	100/0	800-900
Formulation 3	KYNAR®720	ABC1* triblock	85/15	1000-1100
Formulation 4	KYNAR®720	ABC1* triblock	75/25	1100-1200
Control 4	KYNAR®720	CS	75/25	1100-1200
Control 5	KYNAR®720	Plasticizer/CS	75/5/20	900-1000
Control 6	KYNAR®740	ABC1* triblock	100/0	1800-1900
Formulation 5	KYNAR®740	ABC1* triblock	85/15	1900-2000
Formulation 6	KYNAR®740	ABC1* triblock	75/25	2000-2100

CS: Commercial core/shell material, called EXL 3600, used as an impact modifier
Plasticizer: dibutyl sebacate.

Processing of the tubes:

The granules coming from the compounding operation are processed on a conventional coextruder at a temperature of 230°C in order to produce trilayer tubes. This technology is described in many articles, for example, "Plastics Extrusion Technology", Edited by F. Hensen, 1988, 738 pages, ISBN: 0-19-520760-2).

The outer layer consists of MA4411 PA-12, the composition of which was described above, and has a thickness of 750 μm.

The intermediate layer consists of a PVDF-based binder denoted as Binder 1, the composition of which was described above, and has a thickness of 50 μm.

The internal layer (in contact with the petrol) consists of the formulations described in Table I and has a thickness of 200 μm.

The haul-off rate is 15 m/minute.

The characteristics of the various tubes produced are given in Table II.

Table II

Trilayer tubes produced: outside diameter 8 mm; thickness 1 mm.

Structure	Thicknesses of the layers (μm)	Coextrusion* Haul-off rate (in m/min.)	GM 213M** impact results at – 40°C
PA-12/Binder 1/Control 1	750/50/200	15	10/10
PA-12/Binder 1/ Formulation 1	750/50/200	15	0/10
PA-12/Binder 1/ Formulation 2	750/50/200	15	0/10
PA-12/Binder 1/Control 2	750/50/200	15	10/10
PA-12/Binder 1/Control 3	750/50/200	15	10/10
PA-12/Binder 1/ Formulation 3	750/50/200	15	0/10
PA-12/Binder 1/ Formulation 4	750/50/200	15	0/10
PA-12/Binder 1/Control 4	750/50/200	15	8/10
PA-12/Binder 1/Control 5	750/50/200	15	6/10
PA-12/Binder 1/PA-12	750/50/200	15	0/10
PA-12/Binder 1/Control 6	750/50/200	10	N.D.
PA-12/Binder 1/ Formulation 5	750/50/200	10	N.D.
PA-12/Binder 1/ Formulation 6	750/50/200	7	N.D.

N.D. means Not Done.

*: when the coextrusion can be carried out under industrial conditions (at a haul-off rate of 15 m/minute), the tube obtained is of good quality. On the

other hand, when the formulation is too viscous (> 1500 Pa.s), it is necessary to reduce the haul-off rate and the tube obtained does not have satisfactory dimensional characteristics.

**: the GM impact results are expressed as the number of tubes broken or cracked per ten tubes impacted. The standard stipulates that a structure passes the GM 213M impact test if there is no break or cracking for ten tubes impacted (0/10), otherwise the structure is not regarded as satisfactory. It is important to note that a fine crack cannot be detected with the eye. The standard stipulates that the burst pressure of the tube be measured before and after the impact test. In order for a tube to pass the test, it is necessary for the burst pressure after the impact to be at least equal to 80% of the value of the burst pressure measured on the tube before the impact test.

Table III

Static permeability to M15 petrol at 60°C, carried out on films 200 μm in thickness (the M15 petrol is composed of 15% methanol, 42.5% toluene and 42.5% isooctane)

Film No.	Polymer blend or control polymer	Permeability in g/m^2.24 hours, measured and then calculated for a film thickness of 1 mm
1	KYNAR®720/ABC1* (85/15)	13
2	KYNAR®720/ABC1* (80/20)	23
3	KYNAR®720/ABC1* (75/25)	35
4**	PA-12	473
5**	EVOH	36

** Control films for comparison

Comments:

The trilayer tube produced from formulation Control 1, the internal layer of which is made of KYNAR®710, does not withstand the – 40°C GM impact test. On the other hand, the tubes produced under the same conditions from blends containing 15% and 25% of ABC1* triblock respectively, withstand the – 40°C GM impact test. This particular impact withstand cannot be attributed merely to the PS-PB (BC1) diblocks present in the ABC1* product, as the result of the impact test carried out on the tube made from Control 2 shows. We therefore state that this

particular impact withstand is due to the presence of the PMMA-PB-PS triblocks described above.

The tests carried out by replacing the KYNAR®720 with KYNAR®710 illustrate the same result: the Control 3 breaks while Formulations 3 and 4 based on a ABC1* triblock do not. Furthermore, additional tests were carried out by adding to the PVDF either core/shell material alone (Control 4) or core/shell material and plasticizer (Control 5). These additives are known to greatly improve the low-temperature impact strength of PVDF. Surprisingly, we find that the structures produced from these two controls do not withstand the – 40°C GM impact test. Furthermore, adding plasticizer is in any case not desirable since the plasticizer is extracted by petrol.

The PA-12/Binder 1/PA-12 trilayer tube exhibits very good – 40°C GM impact behaviour – none of the tubes breaks. In this regard, it is as satisfactory as the formulations claimed in the present invention. However, the internal layer (in contact with the petrol) is in this case made of PA-12, and this polymer is much less of a barrier to petrol than the claimed formulations as demonstrated by the permeability results given in Table III (PA-12 is 15 to 30 times more permeable than the claimed compositions). In addition, a polyamide always contains oligomers (and in this specific case, some plasticizer), these products being extracted by petrol. The multilayer structure therefore contains extractables, which is not satisfactory for the application.

Control 6 and Formulations 5 and 6: The viscosity of these products is not suited to thin-tube coextrusion with an outside diameter of 8 mm and a thickness of 1 mm under industrial conditions. On the other hand, this type of composition could be used for producing different structures, and especially larger or thicker tubes.

In all cases, the adhesion between the internal layer (the claimed formulation in the present invention) and the binder layer is perfect.

These results demonstrate that it is possible with the formulations described in the invention to produce multilayer (particularly, trilayer) structures which withstand the – 40°C GM 213M impact test, the petrol-contacting layer of which consists very largely of PVDF, and which maintains excellent petrol-barrier behaviour.

In the examples mentioned in this patent, the thicknesses of the various layers of the tubes have been kept constant; however, these thicknesses may vary. In order to specify the characteristics of the trilayer tubes which can be produced within the scope of this invention, mention may be made of the ranges in which the thicknesses may be chosen:

- Layer 1 made of PVDF + triblock: from 25 to 400 μm, advantageously between 50 and 300 μm and preferably from 75 to 200 μm;

- Layer 2 of binder, a layer providing excellent adhesion between Layer 1 and the PA outer layer: from 10 to 200 μm and preferably from 25 to 100 μm;

- Layer 3 made of PA: the balance, in order to obtain the desired final thickness of the wall of the tube.

The structure is not necessarily a trilayer structure: it may only have 2 layers, the adhesion between the two layers then being provided by the addition of a functional acrylic compound to the layer of PVDF + triblock or else by choosing an ABC triblock capable of ensuring good adhesion to polyamides.

Examples of 2-layer structures and bilayer tubes are:

a) PA/fluoropolymer + ABC triblock + functional acrylic compound;

b) PA/fluoropolymer + ABC triblock + functional acrylic compound + electrically conductive carbon black.

Examples of 3-layer structures and trilayer tubes:

a) PA/binder/fluoropolymer + ABC triblock;

b) PA/binder/fluoropolymer + ABC triblock + electrically conductive carbon black.

Examples of 4-layer structures and quadrilayer tubes:

a) PA/binder/fluoropolymer /fluoropolymer + ABC triblock + electrically conductive carbon black;

b) PA/binder/fluoropolymer + ABC triblock/fluoropolymer + ABC triblock + electrically conductive carbon black.

Optionally, the binder layer may also contain ABC triblocks.